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DETERMINATION OF NITROGEN DIOXIDE IN THE AIR. ESTABLISHMENT OF THE NITROGEN DIOXIDE-NITRITE ION CONVERSION FACTOR.

[Opredeleniye soderzhaniya dvuokisi azota v vozdukhe. Ustanovleniye koeffitsienta perekhoda dvuokisi azota v nitrit-ion.]

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DETERMINATION OF NITROGEN DIOXIDE IN THE AIR. ESTABLISHMENT OF THE NITROGEN DIOXIDE-NITRITE ION CONVERSION FACTOR.

The method currently in use to determine the content of nitrogen dioxide in the air (atmospheric and industrial premises) is based on absorption of nitrogen dioxide by a solution of potassium iodide, and the subsequent determination of the nitrite ion formed by the Griss-Illosvaya reagent [2].

The basis of the method is the conversion of sulfanilic acid into a diazo compound by nitrous acid. The compound, reacting with α-naphthylamine, forms a red dye.

The developers of the method took it that nitrogen dioxide is completely converted into the NO_2^- ion when it reacts with potassium iodide

$$2KI + 2NO_2 \rightarrow 2KNO_2 + I_2. \quad (1)$$

But it is a known fact that the reaction can proceed in other directions, such as the following, when nitrogen dioxide reacts with aqueous solutions

$$3NO_2 + H_2O = 2HNO_3 + NO, \quad (2)$$

$$2NO_2 + H_2O = HNO_2 + HNO_3. \quad (3)$$

So of much more practical interest is an explanation of the degree to which nitrogen dioxide is converted into the nitrite ion when gas-air mixtures are sampled in a potassium iodide solution.

Establishment of the conversion factor of NO_2 to the NO_2^- ion through experiment is greatly complicated by the lack of adequately reliable methods

for obtaining the specified, very small, concentrations of nitrogen dioxide in the air. The difficulty stems primarily from the extremely low boiling point of nitrogen dioxide (20.7°C), so that the use of known liquid vapor metering devices for this purpose are ruled out.

Gas metering devices are not suitable in this particular case either because the calculation of weight concentrations based on measurement of volumes of nitrogen dioxide vapors is highly inaccurate, the result of the partial dimerization of NO_2 to N_2O_4.

Another difficulty is the lack of the required sensitivity on the part of methods usually used to measure very small flows of the substance being metered.

These difficulties in obtaining accurate metering apparently can be explained by the fact that data provided by the various researchers who have studied this question as it pertains to the absorption of gas by Saltzman's reagent differ substantially. Saltzman claims the magnitude is 0.72 [5], whereas Buch and Stratmann [4], as well as Hartkamp [3], assert that the stoichiometric factor is 1.00.

It should be noted that indirect methods were used in all studies cited, as well as in many others, to measure the magnitudes of the concentrations given.

It seems obvious that a direct evaluation of the quantity of NO_2 introduced into the flow of air bubbled through the absorption solution would have yielded more reliable results.

This study used an already developed diffusion type metering device in which the quantity of air introduced into the vapor flow can be measured

directly from the decrease that takes place in the volume of liquid in a calibrated glass capillary. The measuring microscope used to evaluate liquid loss was able to determine with a high degree of accuracy extremely small changes in the quantity of liquid [1].

Figure 1. Metering device for vapors of volatile liquids. 1 - capillary; 2 - polyfluoroethylene resin tip; 3 - calibrated capillary; 4 - metered liquid; 5 - metering device body; 6 - protective ampoule; 7 - rubber stopper.

The metering device used (Figure 1) was a ⌐ - shaped glass tube with a drawn end. The diffusion cell used was a glass capillary, one end of which was sealed. The capillary was filled with liquid nitrogen dioxide and capped with a polyfluoroethylene resin tube.

The use of this cap, which in this case projected into the field of the diffusion barrier, permitted working with liquid nitrogen dioxide without danger of its escaping from the capillary, even if the boiling point were exceeded, and thus simplified adjustment of the liquid evaporation rate. Adjustments were made by increasing, or decreasing, the height of that part of the cap that extended above the capillary.

The high diffusion resistance of the polyfluoroethylene resin, which was considerably greater than that of the capillary, made the evaporation rate independent of the quantity of liquid, an important factor when using metering devices of this type.

Tubes for the alcohol thermometers were used in the metering device. These tubes had the required diameter of 0.2-0.5 mm, and little taper.

The weight method, in terms of mercury, was used to calibrate the capillary, as follows. A section of a capillary tube 10 cm in length was sealed off at one end and vacuum-filled with mercury. This was done by submerging the open end into a test tube containing a layer of mercury on the bottom and which was then evacuated. The creation of the vacuum caused the mercury to fill the capillary, forming a column 60-70 mm high, and corresponding to the working zone. The mass of mercury in the capillary was determined by the difference in weights before and after filling. Dividing by the height of the mercury column yielded the mass of mercury per 1 mm of capillary height. Measurements were repeated three times, and the mean was determined.

The mass of liquid nitrogen dioxide incoming per mm of capillary height was calculated by using the following formula

[illegible] ug/mm,

where

d_{NO_2} is the density of the liquid nitrogen dioxide at 20°C, equal to 1.42 g/cm^3;

d_{Hg} is the density of the mercury at 20°C, equal to 13.547 g/cm^3;

P is the mass of mercury incoming per mm of capillary height (mg/mm).

The capillary was filled with nitrogen dioxide as described for mercury, the only difference being that the test tube of liquid NO_2 was placed in a beaker containing a calcium chloride solution cooled to -5°, -9°C.

The capillary filled with nitrogen dioxide was tightly capped by a polyfluoroethylene tube and by the stopper in the sealed section of this same capillary. The capillary was placed in a centrifuge and the liquid was distilled to the sealed end of the calibrated capillary.

A mark was made in direct proximity to the meniscus on the surface of the capillary with indelible ink. The capillary prepared in this manner then was left to stand in the air for 3-4 hours in order to establish the equilibrium process involved in the diffusion of the nitrogen dioxide through the wall of the polyfluoroethylene resin tube. The capillary then was placed on the microscope stage with the mark up, and the distance from the meniscus to the mark was measured. Capillary temperature, and the time, were recorded simultaneously.

The capillary then was inserted in the body of the metering device, which now was stoppered and placed in a temperature controlled bath, the water of which was at ambient temperature and maintained so at $\pm 0.1°C$. The metering device then was connected to a compressed air source, to an MK-2 microcompressor, for example. This started a slow speed (1-5 ml/min) flow of air through the instrument. This air flow picked up the nitrogen dioxide diffusing through the polyfluoroethylene resin and transported it through the drawn end of the metering device.

The nitrogen dioxide evaporation rate after the metering device had been in use for several hours (up to 24 hours) was determined by withdrawing the capillary and once again measuring the distance from the mark to the meniscus. Its temperature was recorded for the second time.

The difference between the first and second measurements yielded the decrease in the length of the column of liquid, which then was converted into weight units. Taking the thermal expansion of the liquid NO_2 into consideration, the decrease in the length of the column of nitrogen dioxide in the capillary, reduced to the temperature of the first measurement, will be

$$\quad \quad \quad \

t_1 and t_2 are capillary temperatures at the time of the first and second measurements, respectively, °C;

K is the linear coefficient of thermal expansion for liquid nitrogen dioxide, mm/mm x°;

l is the total length of the column of liquid in the capillary, mm.

We were unable to find a coefficient of thermal expansion for liquid nitrogen dioxide in the literature, so we measured it by conducting special experiments. The linear coefficient of thermal expansion, K, for liquid nitrogen dioxide placed in a sealed glass capillary turned out to be equal to 0.00137 mm/mm x ° at ambient temperature. The rate of evaporation of substance from the metering device (g/min) was calculated by using the formula

where

- is time between measurements, min.

The error in determining the rate of evaporation of NO_2 from the metering device described is made up of two magnitudes; the error in the calibration of the capillary, and the error in measuring the NO_2 evaporation rate. The error in calibrating the capillary was determined by taking the error in the batch of mercury used (0.15%), the error in determining the height of its column (0.4%), and the taper in the capillaries (1%). The total calibration error was equal to

The error in measuring the NO_2 evaporation rate was determined by taking the error in the measurement of the decrease in the length of the

NO_2 column (mean 0.25%), and that of the thermal expansion of the liquid in the capillary. This latter error was a mean of 1% when a correction factor for change in capillary temperature accurate to 1°C was applied.

Accordingly, the total error in determining the evaporation rate was

The experiments designed to determine the nitrogen dioxide-nitrite ion conversion factor were conducted by the free placement of the drawn end of the metering device in the inlet fitting of the absorption instrument, through which air was drawn at a rate of 0.25 liter/min, for the specified time interval. The error in the determination of rate of flow of the diluting air in the case of this method of creating the concentration had no effect on the accuracy of the results of such determination. The NO_2 concentration after dilution by air was 0.09-17 mg/m^3. Different quantities of nitrite ion were accumulated in the solution by changing sampling time.

The results of the determination of the specified quantities of nitrogen are listed in Table 1. The tabulated data show that $75 \pm 2\%$ of the nitrogen dioxide is converted to the NO_2^- ion under the analysis conditions specified, and not 100% as had been accepted previously.

The magnitude found for the coefficient is the integral coefficient, and includes the actual degree of conversion of nitrogen dioxide to the nitrite ion, as well as losses resulting from incomplete absorption. This led to special experiments being conducted to study the completeness of the nitrogen dioxide capture. The experiments were designed to determine

the magnitude of the nitrogen dioxide breakthrough in a second absorption instrument. Table 2 lists the results.

These data show that the breakthrough is small, approximately 1%.

The factor for conversion into the nitrite ion in pure form therefore is 74%.

Table 1

DEGREE OF CONVERSION OF NO_2 TO NITRITE ION UPON CAPTURE IN A POTASSIUM IODIDE SOLUTION

Given NO_2, ug (A)	Number of samples	Found NO_2^-, ug (B)	K = B/A	Statistical criteria: $K \pm S_k$	Confidence limits (t = 0.95)	
			C = 1.9 mg/m^3			
1	23	0.762	0.762	0.762 ± 0.016	0.746	0.778
2	19	1.470	0.735	0.735 ± 0.041	0.694	0.776
3	18	2.241	0.747	0.747 ± 0.016	0.731	0.763
5	15	3.720	0.744	0.744 ± 0.018	0.726	0.762
		K_m = 0.747				
			C = 0.09 - 0.1 mg/m^3			
1	15	0.741	0.741	0.741 ± 0.021	0.720	0.762
2	8	1.504	0.752	0.752 ± 0.029	0.733	0.781
3	7	2.256	0.752	0.752 ± 0.022	0.730	0.774
		K_m = 0.748				
			C = 16.08 - 16.84 mg/m^3			
1	20	0.746	0.746	0.746 ± 0.016	0.730	0.766
2	18	1.502	0.751	0.751 ± 0.025	0.726	0.776
3	18	2.286	0.762	0.762 ± 0.019	0.743	0.783
5	18	3.820	0.764	0.764 ± 0.019	0.745	0.782
		K_m = 0.755				

Table 2

MAGNITUDE OF NO_2 BREAKTHROUGH

Given NO_2, ug	Air flow rate, liter/minute	Found NO_2^-, g		Breakthrough, %
		1st absorption instrument	2d absorption instrument	
10	0.25	7.00	0.07	1.00
		7.02	0.07	1.00
		7.00	0.06	0.86
		7.20	0.07	0.97

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